

The specific heats of the alkali halides and their spectroscopic behaviour—Part V. The evaluation of the frequencies

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In the preceding parts of the memoir, it has been shown that the structure of the alkali halides admits of nine distinct species of normal modes of vibration. The geometric characters common to each species were described and their respective degeneracies were deduced. Explicit formulae were also obtained for the vibrational frequency of each of the nine species of normal modes. To achieve the purposes of the memoir, two further steps are necessary. The first is to evaluate the nine frequencies numerically for each of the sixteen halides with which we are concerned. Only when this is done is it possible to proceed to the computation of their specific heats as functions of the temperature. The second step is to discuss the activities of each species of normal vibration in respect of infra-red absorption and reflection as well as in respect of the scattering of light with altered wavelength. This is necessary to enable the observable spectroscopic behaviour of the respective halides to be predicted or interpreted and the theoretically calculated frequencies of the normal modes to be confirmed experimentally.

We proceed to consider the problem of the numerical evaluation of the frequencies of the normal modes of vibration. A knowledge of all the five force-constants, viz., α , β , γ , ϕ and ψ is clearly necessary to enable these computations to be carried out with all necessary accuracy. The question thus arises, how are these constants to be found? A further difficulty arises from the nature of the formulae which have been obtained. These are simple enough in the case of the principal mode of vibration where the frequency is determined by a simple summation ($2\alpha + 4\beta + 8\gamma$) of the first three force-constants. The formulae are also quite simple in the cases of the four octahedral modes of vibration. The force-constants there appearing are also simple summations, viz., ($2\alpha + 4\beta + 8\gamma + 16\phi$), ($2\alpha + 4\beta + 8\gamma + 4\phi$), ($2\alpha + 4\beta + 8\gamma + 16\psi$) and ($2\alpha + 4\beta + 8\gamma + 4\psi$), respectively in the four cases. However, in the case of the four modes of coupled oscillation of the atoms located in the cubic layers, the formulae appear in a much more complicated form involving all the five force-constants combined in different ways in the four cases. The only practicable procedure in these circumstances appears to be that of

making the computations using only the two constants α and β in the first instance and ignoring the other three, viz., γ , ϕ and ψ . The results thus obtained cannot, of course, be strictly correct and would need subsequent amendment, especially in the case of the octahedral modes where the neglect of the force-constants ϕ and ψ would result in making the normal and tangential vibrations of the atoms in the octahedral layers have the same frequencies. Nevertheless, the simplification proposed is substantially justified, since α and β which express the interaction between adjacent metal and halogen atoms due to their relative displacements would obviously be more important than the interactions between atoms which are much further apart. Further, in thus basing the computations on only the two force-constants α and β , we also simplify the question of finding what the force-constants are.

Before we proceed further, it would be useful to present a table giving the description of the nine modes of vibration, their respective degeneracies, and the simplified formulae for their respective frequencies in which only the two force-constants α and β appear. The last column of table 1 gives the expression for $4\pi^2 c^2 m_h^2 v^2$ where c is the velocity of light, m_h is the mass of an atom of hydrogen, m_1 and m_2 now designate the atomic weights of metal and halogen and v is the frequency of the mode expressed in wave-numbers. The modes have been arranged in the table in the descending order of frequency. It should be remarked, however, that if $m_1 > m_2$, the fourth and sixth entries should interchange places in the table, and likewise also the fifth and the seventh entries.

We have now to find a means of ascertaining the magnitudes of the force-constants α and β . As has already been remarked in part III of the memoir, α is the force-constant for a stretching of the chemical bonds which unite the adjacent metal and halogen atoms in the crystal, while β is the force-constant associated with a change of the bond-angles which in the equilibrium state are all right angles. It is evident that if a cube of the crystal is subjected to pressures of equal magnitude normal to all its six faces, in other words to a hydrostatic compression, all the bond-lengths in the crystal would be diminished in the same proportion, but the bond-angles would remain unaltered. Further, if the crystal were subjected to tractive forces parallel to the cube faces, in other words, to shearing stresses, the bond-angles would be altered, but the bond-lengths would remain the same. Thus, macroscopically regarded, the bulk-modulus of elasticity of the crystal bears to its shear-modulus the same relation that α bears to β in an atomistic picture. Hence, we are justified in assuming that α is related in a very simple manner to the bulk-modulus of elasticity and β to the shear-modulus. If we multiply each modulus by the distance d which separates adjacent atoms of metal and halogen, we obtain quantities having the physical dimensions of the force-constants with which we are concerned. Accordingly we proceed to write $\alpha = K \times d$ and $\beta = C_{44} \times d$ where K and C_{44} for each of the alkali halides have the values listed in part I of this memoir.

We may proceed to test the validity of the foregoing expressions for α and β by

Table 1. Simplified frequency formulae

Description of mode	Degeneracy	$4\pi^2 c^2 m_h^2 v^2 =$
Oscillations of the metal and halogen atoms in opposite phases	3	$\frac{(2\alpha + 4\beta)}{\mu}$ or $(2\alpha + 4\beta)\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$
Coupled oscillations in the cubic layers tangentially	6	$\frac{2\alpha + 4\beta}{2\mu} + \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{16\beta(\alpha + \beta)}{m_1 m_2} \right]^{1/2}$
Coupled oscillations in the cubic layers normally	3	$\frac{2\alpha + 4\beta}{2\mu} + \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{32\alpha\beta}{m_1 m_2} \right]^{1/2}$
Oscillations of the atoms in the octahedral planes normally	4	$\frac{(2\alpha + 4\beta)}{m_1}$
Oscillations of the atoms in the octahedral planes tangentially	8	$\frac{(2\alpha + 4\beta)}{m_1}$
Oscillations of the atoms in the octahedral planes normally	4	$\frac{(2\alpha + 4\beta)}{m_2}$
Oscillations of the atoms in the octahedral planes tangentially	8	$\frac{(2\alpha + 4\beta)}{m_2}$
Coupled oscillations of the atoms in the cubic layers normally	3	$\frac{2\alpha + 4\beta}{2\mu} - \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{32\alpha\beta}{m_1 m_2} \right]^{1/2}$
Coupled oscillations of the atoms in the cubic layers tangentially	6	$\frac{2\alpha + 4\beta}{2\mu} - \left[\frac{(2\alpha + 4\beta)^2}{4\mu^2} - \frac{16\beta(\alpha + \beta)}{m_1 m_2} \right]^{1/2}$
Translations	3	$v_g \rightarrow 0$

working out their consequences in the case of rock-salt for which the values of all the nine frequencies of vibration of the structure have been determined spectroscopically (reference 1). The bulk-modulus K for rock-salt is 2.52×10^{11} erg/cm³ and the shear-modulus C_{44} is 1.275×10^{11} erg/cm³. Multi-

plying these by d , which is half the lattice-constant and is therefore 2.81 \AA , we find $\alpha = 0.709 \times 10^4 \text{ dyne/cm}$; $\beta = 0.359 \times 10^4 \text{ dyne/cm}$. Using these values of α and β and the simplified formulae for the frequencies of vibration given in table 1 of this part of the memoir, we obtain the following results.

Table 2. Calculated and observed frequencies (in wave-numbers) for NaCl

Degeneracy	3	6	3	4	8	4	8	3	6
Calculated frequencies	187	164	146	146	146	117	117	117	91
Observed frequencies	180	150	129	170	157	140	118	110	92

The highest frequency appearing in table 2 is that of the oscillation of the sodium and chlorine atoms in opposite phases. It is 187 cm^{-1} , which expressed as an infra-red wavelength, comes out as 53.5 microns . Since this mode of vibration is strongly infra-red active, we should expect the maximum reflecting power of a rock-salt surface to be at that wavelength. The rest-strahlen reflections of rock-salt as reported by various observers have a peak at about 54 microns , in excellent agreement with the calculated position. Another satisfactory feature is the close agreement between the calculated and observed values of the eight-fold degenerate frequency (117 cm^{-1}) of the oscillation of the chlorine atoms. This oscillation manifests itself, as is to be expected, in the spectrum of light-scattering by rock-salt as a strong sharp line with the double-frequency shift of 235 cm^{-1} . It is indeed the most conspicuous feature in that spectrum.

In making the calculations, we have ignored the force-constants ϕ and ψ . Since they represent the interactions of like atoms at a distance of $d\sqrt{2}$, their neglect is not wholly justifiable. When they are taken into account, the frequencies which have a four-fold degeneracy would be a little higher than the corresponding frequencies which are eight-fold degenerate. This, it will be seen from table 2, is actually the case for the observed values of the frequencies.

Subject to the foregoing remarks, the agreement between theory and experiment manifested in table 2 may be considered to be highly satisfactory. Accordingly, the same procedure will be adopted in the next part of the memoir in respect of all the other halides.

Summary

Simplified formulae involving only two force-constants α and β are given for the frequencies of the nine normal modes. Reasons are given for identifying the two force-constants as being respectively the products of the bulk-modulus and of the shearing modulus of the crystal by the distance between adjacent metal and

halogen atoms. Calculations made on this basis of the nine frequencies of the rock-salt structure exhibit a highly satisfactory agreement with the spectroscopic data.

Reference

1. Raman C V *Proc. Indian Acad. Sci.* A54 253 (1961).